drolysis of the vinyl ether was more difficult than expected, requiring TsOH (15 mol %) and 18 h, and the alcohol 12[18] was obtained in 55% yield, along with a significant amount of phenylfluorenyl alcohol from solvolysis of the product or intermediate.

Mitsunobu coupling[19] (PPh_3, 100 mol %; DMAD, 100 mol %; THF) of benzenesulfonamide **7** and aziridino alcohol **12** afforded the coupled (phenylsulfonyl)anilide **13**, mp 81-84 °C, as a mixture of conformational isomers in 87% yield. At this stage, we anticipated that the para ester group would sufficiently increase the acidity of the tolyl methyl protons of **13** to permit deprotonation and condensation with the aziridino methyl ester. Although such intramolecular condensations to form eight-membered rings are generally quite poor processes, the severe conformational constraints imposed by the fused benzene and aziridine rings were expected to overcome this barrier. In the event, treatment of the Mitsunobu product **13** with KHMDS (500 mol %, THF, -10 to 5 °C) afforded the ketone **14**,[20] mp 220-222 °C, in 52% yield. This completes the synthesis of the core (3*S*,4*S*)-3,4-aziridinobenzo[1,2-*b*]hexahydroazocine nucleus. To complete the synthesis of FR900482, introduction of the carbamoylmethyl group and the remaining functional group manipulations with ketone **14** are being pursued.

Acknowledgment. Michael Carrasco, President's Undergraduate Fellow, provided valuable assistance in the preparation of intermediates.

Supplementary Material Available: Complete experimental details and ^1H and ^{13}C NMR data for numbered compounds in the synthetic sequence (**4**, **5**, **6**, **7**, **10** and its mesylate, **11**, **12**, **13**, **14**) (7 pages). Ordering information is given on any current masthead page.

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[17] Corey, E. J.; Suggs, J. W. *J. Org. Chem.* **1973**, *38*, 3224.

[18] **12**: ^1H NMR ($CDCl_3$) δ 1.74 (q, 1 H, J = 6.6 Hz, H_β), 2.52 (d, 1 H, J = 6.6 Hz, H_α), 3.56 (b d, 1 H, J = 4.5 Hz, H_γ), 3.72 (s, 3 H, CO_2CH_3), 7.14-7.49 (m, 11 H, ArH), 7.71 (m, 2 H, ArH); ^{13}C NMR δ 37.36 (1), 40.39 (1), 51.75 (3), 59.83 (2), 75.15, 119.81 (1), 125.26 (1), 125.95 (1), 126.57 (1), 126.92 (1), 127.24 (1), 127.75 (1), 128.0 (1), 128.56 (1), 128.74 (1), 139.60, 141.11, 142.23, 144.72, 147.79, 169.71.

[19] Mitsunobo, O. *Synthesis* **1981**, 1. A similar application to aliphatic amines has just appeared: Henry, J. R.; Marcin, L. R.; McIntosh, M. C.; Scola, P. M.; Harris, G. D., Jr.; Weinreb, S. M. *Tetrahedron* **1989**, *30*, 5709.

[20] **14**: ^1H NMR ($CDCl_3$) δ 1.96 (d, 1 H, J = 6.6 Hz, H_α), 2.47 (q, 1 H, J = 3.3 Hz, H_β), 3.50 (d, 1 H, J = 14.3 Hz, H_γ), 3.51 (d, 1 H, J = 18.1 Hz, H_{Bn}), 3.56 (s, 3 H, OCH_3), 3.79 (d, 1 H, J = 18.0 Hz, H_{Bn}), 3.93 (s, 3 H, CO_2CH_3), 4.29 (dd, 1 H, J = 3.4, 14.3 Hz, H_γ), 5.29 (d, 1 H, J = 6.6 Hz, CH_2), 5.46 (d, 1 H, J = 6.6 Hz, CH_2), 6.62-7.92 (m, 20 H, ArH); ^{13}C NMR ($CDCl_3$) δ 42.37 (1), 42.53 (2), 45.34 (1), 47.97 (2), 52.36 (3), 56.62 (3), 75.43, 95.10 (2), 115.25 (1), 120.10 (1), 120.31 (1), 121.44 (1), 124.91 (1), 126.35 (1), 126.44 (1), 127.01 (1), 127.18 (1), 127.77 (1), 127.95 (1), 127.99 (1), 128.74 (1), 129.04 (1), 129.26 (1), 129.42 (1), 133.32 (1), 136.35, 138.03, 139.13, 140.47, 142.07, 142.14, 142.55, 147.74, 154.31, 165.79, 204.13.

Reaction of Trithiolanes with Dihalocarbenes under Phase-Transfer Catalysis. A Convenient Synthesis of Trithiocarbonates and Thionocarbonates

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Summary: The reaction of trithiolanes with both dichloro- and dibromocarbene under phase-transfer catalysis has been studied in detail. The primary product is the trithiocarbonate, which undergoes further reaction to give the thionocarbonates. A mechanism for this reaction is discussed.

Recently we reported on the oxidation of norbornane trithiolanes with a variety of reagents.[1] This study indicated that simple norbornane trithiolanes have the potential to serve as good models for investigating trisulfide chemistry. Here we describe the reaction of trithiolanes with dihalocarbenes. Although we have been unable to find any example in the literature on the reactivity of trithiolanes (or trisulfides for that matter) with dihalocarbenes, there are quite a few reports on the reaction with disulfides.

In the earliest study of the reaction of disulfides with carbenes, Searles and Wann found that dichlorocarbene led to (dichloromethyl)alkyl disulfides and alkenes (eq 1).[2]

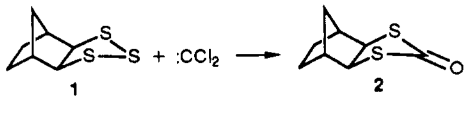
$$(CH_3)_3CSSC(CH_3)_3 + :CCl_2 \rightarrow (CH_3)_3CSSCHCl_2 + CH_2{=}C(CH_3)_2 \qquad (1)$$

Aryl disulfides on the other hand do not react with dichlorocarbene.[3] Recently dichlorocarbene has been shown to act as both as an oxidizing and reducing agent for organosulfur compounds under phase-transfer catalysis.[4,5] With this information in hand the following study was undertaken.

Table I. Ratio of 2 and 3 with Time

time, h	2/3	1, %
0.17	2.9	52
1	2.9	24
7	2.3	16
17	2.3	16

Heating a mixture of *exo*-3,4,5-trithiatricyclo-[5.2.1.0^{2,6}]decane (**1**),[6] excess NaOH and benzyltriethylammonium chloride (TEBAC) in $CHCl_3$ at reflux gave a 60% yield of *exo*-3,5-dithia-4-oxotricyclo[5.2.1.0^{2,6}]decane (**2**)[7] as the only product. If the reaction is carried out at



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[1] Ghosh, T.; Bartlett, P. D. *J. Am. Chem. Soc.* **1988**, *110*, 7499-7506.

[2] Searles, S., Jr.; Wann, R. E. *Tetrahedron Lett.* **1965**, 2899-2902.

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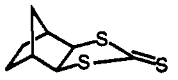
room temperature and monitored by gas chromatography (Table I), the formation of a second product is observed. This product could be isolated and purified by preparative gas chromatography and was identified as the norbornanetrithiocarbonate **3**.[8]



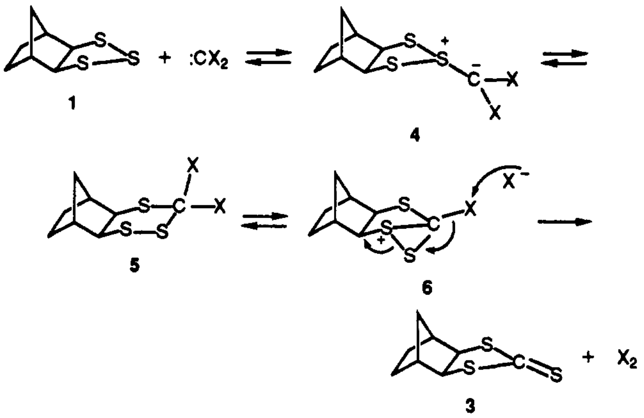
3

In a control experiment a pure sample of **3** in CD_2Cl_2 was stirred with NaOH and TEBAC. ^{1}H NMR spectroscopy indicated no change had occurred. Therefore **2** is not formed from **3** by hydrolysis due to water carried by NaOH (or TEBAC). A few drops of $CHCl_3$ was then added and stirring continued. Within a few hours the reaction mixture had turned brown, and both GC/MS and the ^{1}H NMR spectrum showed that **3** was no longer present. The only product that could be identified was **2** (yield, 50%). This result indicates a chain of events in which **3** is formed initially and then undergoes further reaction with dichlorocarbene to produce **2**.

When **1** was stirred with NaOH, TEBAC, and a 3-fold excess of $CHBr_3$ in CH_2Cl_2 for 4 days gas chromatography showed **3** to be formed in a large excess over **2** ($3/2 = 5.5$). On the other hand if the above experiment is repeated with a large excess of $CHBr_3$, after 4 days **2** is found to be the major component ($3/2 = 0.12$). Thus in the dibromocarbene reaction the formation of **3** from **1** is much faster than the formation of **2** from **3**, while the reverse is true in the dichlorocarbene reaction.

A plausible mechanism that may explain the formation of **3** from **1** is shown in Scheme I. We have previously shown that ozone preferentially attacks the middle sulfur atom over the terminal sulfur atoms.[1] Thus an electrophilic dihalocarbene would react with **1** to give initially the ylid[9] **4**, which could then undergo bond rearrangement to give the neutral species **5**. Once **5** is formed the nucleophilicity of sulfur and the propensity of X as a leaving group takes charge, giving **3** via the sulfonium intermediate **6**. How **3** is converted to the thionocarbonate **2** by reaction with a dihalocarbene we do not known at this time.

Scheme I



Evidence that our proposed mechanism may be operative came from a trapping experiment. When the reaction of **1** with dibromocarbene was carried out in the presence of cycloheptene we were able to isolate a considerable quantity of 1,2-dibromocycloheptane. Interestingly enough, no dibromocarbene adduct of cycloheptene could be observed either by GC/MS or ^{1}H NMR spectroscopy. Although this does not prove the entire mechanism, there is no doubt that bromine (and probably chlorine in the case of dichlorocarbene) is being generated. Studying this reaction by generating dihalocarbenes from other sources and by using other disubstituted carbenes will throw more light on this reaction. Future reports will deal with these experiments.

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